Effect of TiO_2 on Electrical Properties of $ZnCr_2O_4$ Synthesized by Conventional Ceramic Route

This thesis is submitted in partial fulfillment of the requirement for the degree of

Master of Science in

PHYSICS

By

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ROURKELA

CERTIFICATE

This is to certify that the thesis entitled "Effect of TiO_2 on Electrical Properties of $ZnCr_2O_4$ Synthesized by Conventional Ceramic Route**"** submitted by RojaliNayak in partial fulfillments for the requirements for the award of the degree in Master of Science in Physics, National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in this project has not been submitted to any other University/ Institute for the award of any degree in M.Sc. Physics.

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21.06.2013 ROJALI NAYAK

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Abstract

The electrical properties of ZCO-TO composite are studied properly by analysing the impedance data taken at RT within frequency windows of 100 Hz to 1 MHz. The presence of TO particles in the matrix of ZCO is confirmed from XRD study as it contains the peaks of both compounds. This indicates the formation of desired composite. SEM image shows the grain growth with percentage addition of TO. The size of the grain has put impact on the electric properties of the composite observed from impedance study. The impedance value decreases up to 40% addition of TO and then it increases again. Nyquist plots show the co contribution of grain and grain boundary with the electrode effect contributes towards conduction and polarisation mechanism.Space charge polarisation is responsible for rise in relative permittivity value.

CHAPTER-1

INTRODUCTION

1.1 MOTIVATION AND BACKGROUND:

Oxides with "spinel" structure are some of the most studied compounds in solid-state sciences due to interesting physico-chemical properties and found useful in many technological applications such as magnetic materials, super hard materials, and high-temperature ceramics.
Metal oxides have been an extremely active field and have been widely studied in recent years. Spinel oxides are a family of complex metal oxides. Spinel oxides are of special importance for luminescence materials, magnetic materials, sensors, catalysts, and lithium batteries. A large group of ceramic materials is formed by spinels, which can be treated as double oxides of the composition $A^{2+}B^{3+}{}_2O_4$.

Spinel and spinel-like oxides are attractive subjects for continuousscientific interest and have been deeply investigated in materials sciences, because of their physico-chemical properties. They have found wide applications as refractory materials, catalysts, and supports of catalytically active phases for various reactions.

Due to environmental and economic concerns, the development of highly efficient catalytic processes minimizing the formation of side products and residues. An interesting approach is that the supporting system of catalytically active metals on molecular sieves and related systems, thus it enhancing the selectivity, because of the well-defined porous system.

According to Price et.al and Robbins et al cation arrangement in spinel-type oxides has long been a topic of interest among mineralogists because the site distribution (particularly of iron) has a strong effect on magnetic, electrical and thermochemical properties.Studies of a variety of end member spinel compositionand binary solid solution have brought into focus many problems concerning the compositional dependence of cation distribution in spinels.

Dielectric:

Dielectrics are materials which have no free charges; all electrons are bound and associated with the nearest atoms. An external electric field causes a small separation of the centers of the electron cloud and the positive ion core so that each infinitesimal element of volume behaves as an electric dipole. When a sufficient magnitude of electric field is applied to the crystal the the positive charges within the dielectric are displaced in small time in the direction of the electric field, and the negative charges are displaced minutely in the direction opposite to the electric field. This slight separation of polarization reduces the electric field within the dielectric field.

Polarization:

The Polarization is defining itself as the dipole moment per unit volume at a given point.

$$P = Np$$

Where p is the average dipole moment of molecule, and N is known as the number of molecules per unit volume.

The type of polarization are additionally divided into the following categories such as

1. Electronic polarization –where a displacement of the electronic cloud w.r.t the nucleus occurs.

2. Ionic polarization: Here separation of +ve and -ve ions in the crystal occurs

3. Orientation polarization: The alignment of permanent dipoles or molecules occurs.

4. Space-charge: In this polarization the free electrons are present but are prevented from moving by electrode such as grain boundaries.

Cole–Cole plot:

A widely used graphical representation of frequency- dependent complex dielectric functions $\varepsilon(w) = \varepsilon(0)$ for various materials is the well-known Cole- Cole plot, in which ε'' is plotted on the vertical axis against ε'. The Cole-Cole plot is particularly useful for materials which possess one or more well separated relaxation processes with comparable magnitudes and obeying the Debye or Cole-Cole functional forms. For instance for a Debye relaxation process the Cole-Cole

plot reduces to a semicircle. However, when the material also possesses a conductivity, the Cole-Cole plot becomes less useful, because the presence of a dc conductivity leads to a divergence of ε'' at low frequencies.

1.2 INTRODUCTION TO $ZnCr_2O_4$:

Zinc chromite ($ZnCr_2O_4$) is a mixed oxide which crystallizes in the cubic system and has a normal spinel structure. Non-magnetic Zn^{2+} and magnetic Cr^{3+} ions have a strong preference for the tetrahedral and the octahedral B-sites, respectively. $ZnCr_2O_4$ is a geometrically frustrated antiferromagnetic with a first order transition at12.5 K from paramagnetic phase with cubic structure to antiferromagnetic phase with tetragonal structure. $ZnCr_2O_4$ is very attractive as air depollution catalytic material, for a variety of reaction like oxidation of hydrocarbons, oxidative dehydrogenation of hydrocarbons, synthesis of methanol as photo catalyst gas sensing and humidity sensing.With a normal spinel structure (AB_2O_4), $ZnCr_2O_4$ has the crystal group Fd3m with lattice constants of a=58.280 A $^{\circ}$. Zn^{2+} and Cr^{3+} ions occupy mainly the tetrahedral and octahedral positions, respectively according to their ionic radii.

Spinels oxides such as $ZnCr_2O_4$ which contains transition metal ions can act as the efficient catalysts in the number of heterogeneous chemical processes such as CO oxidation, catalytic combustion of hydrocarbons, reduction of several organic molecules and sensing properties.

1.3 INTRODUCTION TO TiO_2:

TiO_2 powders have been commonly used as white pigments from ancient times. These are inexpensive, and also chemically stable and harmless, and have no absorption in the visible region. They haveunique properties and several potential technological applications such as in photo catalysis, sensors, solar cell and memory devices etc. TiO_2 exists in three polymorphic phases such as rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Both anatase and rutile structure have tetragonal crystal structures but they belong to different space groups. Among the above three crystal structures of TiO_2, anatase structure owing to its higher photo catalytic activity which is commonly used for photo catalysis. This higher photo catalytic activity is related to its lattice structure. Each Ti atom is coordinated with six oxygen atoms in the

anatase tetragonal unit cell. Yong et.al has reported a significant degree of buckling associated with O-Ti-O bonds in anatase structure compared to rutile structure of TiO_2. The titanium and oxygen atoms are more tightly packed in the rutile crystal. Both anatase and rutile structures can also be described in terms of chains of TiO_2 octahedral. Here Each Ti^{+4} ions are surrounded by an octahedron of six O^{-2} ions. TiO_2 is stable in aqueous media and is tolerant of both acidic and alkaline solutions. It is generally inexpensive, recyclable, and reusable and relatively simple to produce. Titanium oxide is transparent and more effective as UV absorbers and photo catalysts. The transparency and UV absorbance allow for effective use in protective ingredient for sunscreens.

CHAPTER-2

LITERATURE REVIEW

2.1 SPINEL STRUCTURE OF $ZnCr_2O_4$:

In solid-state science, oxides with spinel structures are some of the most studied compounds due to their wide range of applications. Spinel is an important class of mixed-metal oxides, which has the general composition of AB_2O_4. Spinel's most simple symmetry can be described by a cube with a lattice point at each of its eight corners as well as a lattice point on each of the 6 faces. So we called this symmetry as face centered cubic (fcc).The spinel structure is named after the mineral spinel ($MgAl_2O_4$); the general composition is AB_2O_4.Normally A is a divalent atom which has of radius in between 80pm and 110pm, such as Mg, Fe, Zn, and Cu. and B is a trivalent atom which has of radius in between 75 and 90pm, such as Ti, Fe, Al, and Co.The structure consists of a cubic closed-packed array of 32 oxide ions, which forms 64 tetrahedral sites and 32 octahedral sites in one unit cell (AB_2O_4).The cations occupy 1/8 of the tetrahedral sites and 1/2 of the octahedral sites and there are 32 O-ions in the unit cell. There are two types of sub-cells commonly described for the spinel structure, here shown is a structure a and structure b in Figures 1-a and 1-b respectively. Structure 1-a: shows that the filling of the 2 tetrahedral sites within one-eighth of the unit cell, and structure b shows a filled octahedral site. There are 12 filled octahedral sites not centered in the sub-cells that are also are located in half the octahedral sites, while all the divalent cations occupy 1/8 of the tetrahedral sites.

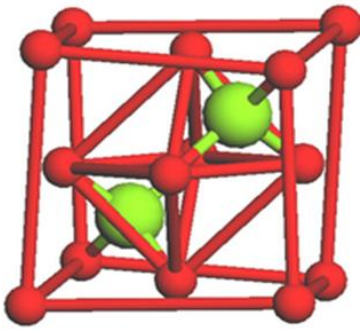


Figure 1-a: Two types of occupied tetrahedral sites in spinel sub-cell.

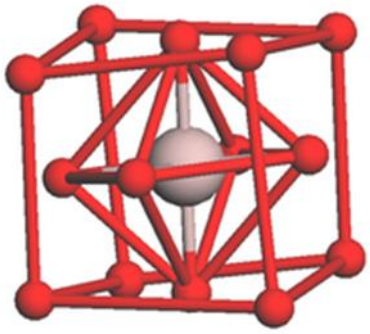


Figure 1-b: Occupied octahedral site in spinel sub-cell b.

The spinel structure is also interesting because it may contain vacancies as regular part of the crystal. One example is that, if the magnetite is slowly oxidized by lying around a couple of billion years, or when rocks cool, (Fe^{2+} will turn into Fe^{3+}.). If the Fe^{2+} is converted into the Fe^{3+}, then the charge balance requires a formula of Fe21, 67O32 per each unit cell and this means that the 2,33 sites must be vacant. Spinels can be classified as either normal spinel structure or inverse spinel structure; it depends upon the cation distribution. The arrangement of the above two cubic sub-cells in one unit cell is shown in Figure (2).An inverse spinel is an alternative arrangement where the divalent ions swap with half of the trivalent ions so that the M(II) now occupy octahedral sites i.e. B (AB) O4.an inverse spinel structure is effectively the opposite of a normal spinel structure. The structure of an inverse spinel occurs primarily because certain types of ions with a positive two charge naturally prefer to be in an octahedral and they force the positive-three charge ions out. One example of this inverse spinel structure is Mg_2TiO_4.

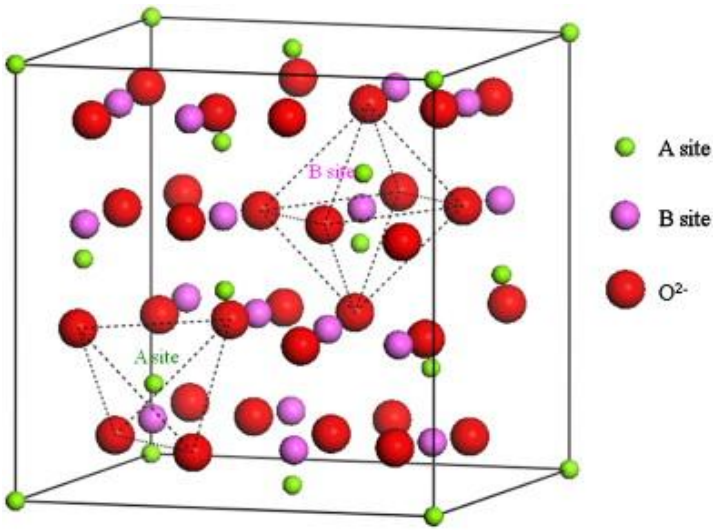


Figure 2: Diagrammatic sketch of spinel crystal structure.

2.2 OPTICAL PROPERTIES OF ZnO:

Semiconductor compounds have drawn much attention during the last few years because of their novel optical and transport properties which have great potential for many optoelectronic applications. ZnO is found to be a wide band gap semiconductor that displays high optical transparency and luminescent properties in the near ultra violet and the visible regions. Due to these properties ZnO is a promising material for electronic and optoelectronic applications such as solar cells (anti-reflecting coating), gas sensors, liquid crystal displays (LCD), surface acoustic wave devices etc. ZnO is a wide band gap semiconductor of about 3.37 eV which corresponds to emission in the UV region. This band gap ofZnO is very nearer to the GaN (3.39eV), and GaN has been the subject of much research over the past years. However, ZnO has some significant advantages in its large free exciton binding energy (60 meV) that allows for efficient excitonic emission at room temperature. For material science applications, zinc oxide also found to be have high refractive index, high thermal conductivity also, binding, and UV-protection properties.

2.3 OPTICAL PROPERTIES OF TiO_2:

Titanium oxide (TiO_2) is a material with wide application due to its optical and electronic properties Titanium dioxide has excellent properties such as high optical transmittance, high refractive index, and better durability.TiO_2 is the promising material as semiconductor having high photochemical stability and low cost.In TiO_2, the crystalline phase, the composition and the surface states strongly affect the electronic structure and the charge properties. The photo catalytic activity of TiO_2 depends on its present phase. There are three crystalline forms of TiO_2: anatase, rutile and brookite. Anatase phase is metastable and has the greater photo catalytic activity; rutile has a high chemical stability but is less active. Besides, some TiO_2 with a large quantity of anatase and a small quantity of rutile exhibits a higher photo catalytic activity than in the pure anatase or rutile phases. The majority of authors have determined that in TiO_2 the rutile structure has a direct band gap of 3.06 eV and an indirect band gap of 3.10 eV and the anatase structure has only one indirect band gap of about 3.23 eV.Titanium dioxide (TiO_2), an oxide semiconductor, is considered as a suitable material for various photo catalytic applications because of its strong oxidizing power, high chemical inertness, low cost, and long-term stability. However, a large band gap (3.2 eV) of anatase TiO_2 restricts its use only to the narrow light-response range of ultraviolet.

2.4 OPTICAL PROPERTIES OF Cr_2O_3:

Chromium oxide is an insulating antiferromagnetic property. It is also suitable as a tunnel junction barrier. Chromium oxide Cr_2O_3 are of great interest due to their wide variety of technological applications. This oxide exhibit high hardness and high wear with corrosion resistance which are important properties for protective coating application sit has already found several applications as protective coatings on read–write heads in digital magnetic recording units and in gas-bearing applications.. This form of oxide has important industrial applications, for instance in catalysis and solar thermal energy collectors. It has a band gap of 3.3 eV.

2.5 APPLICATION OF $ZnCr_2O_4$:

Spinels such as $ZnCr_2O_4$ containing transition metal ions can act as the efficient catalysts in the number of heterogeneous chemical processes such as CO oxidation ,catalytic combustion of

hydrocarbons, reduction of several organic molecules, and sensing properties. Zinc chromite ($ZnCr_2O_4$) is useful catalysis materials for air pollution control, synthesis of alternative fuel, and sensor materials. A combination set of $Cu_2O/ZnO/Cr_2O_3$ catalyst is extensively used in CO emission control for automobile. ZnO is an n-type semiconductor oxide, capable of donating electrons, while Cr_2O_3 is a p-type oxide, capable of extracting electrons. But both are good for hydrogenation catalyst. Zinc spinels are commonly found as accessory minerals in a wide range of rocks in the Earth's crust. Furthermore, spinels have also found frequent application in materials science. For example, zinc chromite ($ZnCr_2O_4$) spinels are commonly used as catalytic materials (Gabr et al., 1992; Beretta et al., 1996) and as humidity sensors.

Objective of the Study:

- Zinc Chromites and Titania has been studied a lot for their attractive optical properties as both are good visible light photo catalyst. The electrical transport properties have not been rigorously studied yet. Therefore the present work dealt with an objective….
- To synthesize ZCO-TO composites of different proportions and investigate their electrical properties through complex impedance technique.

CHAPTER-3

EXPERIMENTAL METHODS

This chapter consists of different type of synthesis and characterization techniques of

(1-X)$ZnCr_2O_4$ -$XTiO_2$ composite such as:

1. Synthesis of (1-X) $ZnCr_2O_4$ –$XTiO_2$ composite by solid state reaction route.

2. Characterization with different techniques of different composites.

3.1 DIFFERENT SYNTHESIS TECHNIQUES:

There is several synthesis methods are available such as;

- **Solid state reaction method**
- **Sol-gel method**
- **Auto –Combustion method**
- **Co-precipitation method**

Solid state reaction method:

This is the most widely used method for the synthesis of polycrystalline bulk materials. Since, solids do not react with each other at room temperature, it is necessary to heat them at elevated temperatures as high as up to 1500 ^oC for the proper reaction to take place at appreciable rate. Thus, both, thermodynamic and kinetic factors are important in Solid State Reaction. In SSR method, the solid reactants react chemically without the presence of any solvent at high temperatures yielding a product which is stable. The major advantage of SSR method is, the final product is structurally purein solid form with the desired properties depending on the final sintering temperatures. This method is environment friendly and no toxic or unwanted waste is produced after it is complete.

Sol-gel method:

Sol - Gel is a chemical solution based process of synthesizing wide range of materials especially mixed oxides which is used due to its advantages of flexible nature, low temperature synthesis etc. The control on stoichiometry of the resultant product is benefit of this method. A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. A gel consists of a three dimensional network, which can enclose the liquid phase, in a colloidal form of gel, the network is consists of agglomeration of colloidal particles.

Sol - Gel method has been widely used in synthesizing not only glasses and ceramics but also organics and biomaterials. It also provides better results for inorganic as well as organic compositions. It offers homogeneous particle growth having small size, uniform size distribution and mono dispersive nature of the particles. Sol-gel method is very easy for handling and in set-up, cost-effective and yields predefined stoichiometric compounds.

Co-precipitation method:

In conventional synthesis routes, the reactants are mixed together by grinding the mixture of starting materials or mechanically by ball milling process and the subsequent reaction rate depends on a large degree on the particle size of the reactants, the degree of homogenization achieved on mixing and the intimacy of contact between the grains, as well as the obvious effect of temperature. By using the co-precipitation route, it is possible to achieve a high degree of homogenization together with a small particle size and faster reaction rates.

The extent to which a component can be separated from solution can be determined from the solubility-product constant obtained by determining the quantity of dissolved substance present in a known amount of saturated solution. This value is known as the solubility. The solubility can be instantly altered merely by adding to the solution of any ions which make up the precipitate. Although, solubility can be altered over a wide range, the solubility product itself remains practically constant over the same range.

Auto-combustion method:

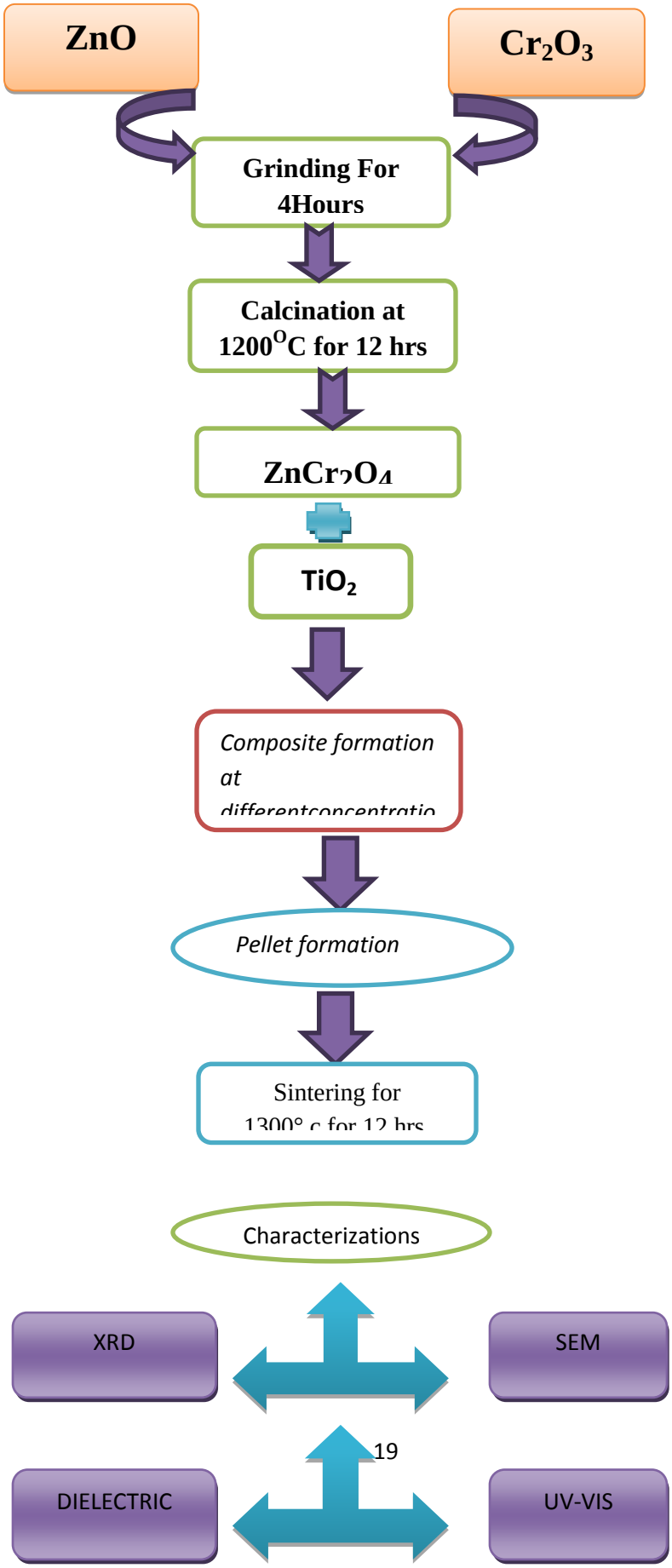
Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, inexpensive method for the production of various industrially useful materials. Today combustion synthesis has become a very popular approach for preparation of nanomaterial's and is practiced in 65 countries. Recently, a number of important breakthrough in this field have been made, for development of other new catalysts and Nano carriers with properties better than those for similar traditional materials

From Above different synthesis root here it is used solid state reaction method. In this method first formation of powder with stoichiometric relation then it goes for grinding for 4 hr. Then for getting desired phase formation it is gone for calcination, the pellet preparation with PVA and sintering at 1300^{o}Cfor 6 hr. below the melting point.

The different synthesis techniques that have been done are:

- Powder formation
- Grinding
- Calcination
- Pellet formation
- Sintering

3.2 FLOW CHART FOR MATERIAL SYNTHESIS:



3.3 EXPLANATION OF SYNTHESIS METHOD BY SOLID STATE REACTION ROUTE METHOD:

Solid State Reaction Route is a synthesis process used for the preparation of polycrystalline ceramic materials. Solid State Reaction route provides large ranges of selection of starting materials like, oxides, carbonates, etc. As solids do not react with each other at room temperature it is necessary to heat them at elevated temperatures as high as up to 1500 ^{o}C for the proper reaction to take place at appreciable rate. Thus, both thermodynamic and kinetic factors are important in solid state reaction route. The major advantages of Solid State Reaction route are, the final product in solid form is structurally pure with the desired properties depending on the final sintering temperatures. This method is environment friendly and no toxic or unwanted waste is produced after the SSR is complete. Details of the synthesis procedure are as follows.

1. Grinding:

After weighing the sample with required amounts the chemicals are mixed. For manual mixing of small amounts or quantities usually an agate mortar and pastel are employed. For quantities greater than 20 gm. mechanically mixing usually adopted such as ball milling which takes only few hours.

2. Calcination:

Calcination is the heating of a substance to high temperature, but below the melting point of material to bring about thermal decomposition. It is mainly thermal treatment process and applied to ores and other solid materials to bring

a) Thermal decomposition

b) Phase transition and

c) To remove volatile fractions such as CO_2 H_2O

Material is heated below the melting point in rotary kiln or fluidized bed reactor. Calcination is done in the solid state. Here the zinc chromite powder was calcined at 1200 ºC.

3. Mixing of TiO_2 with $ZnCr_2O_4$:

$ZnCr_2O_4$ –TiO_2 composites are prepared by mixing the different concentration of TiO_2 with the $ZnCr_2O_4$ with the formula (1-X) $ZnCr_2O_4$-$XTiO_2$ where x=0.2, 0.3, 0.4, 0.5.

4. Pelletization:

After calcination, the composites powders are mixed with PVA and grinded about 3-4 hours. Then the pellets are formed from the powders with a load of 5 ton.

5. Sintering:

Sintering is a method for making objects from powder, with heating of the material in a sintering furnace below the melting point (solid state sintering) until its particles adhere to each other. Sintering is also used for manufacturation of ceramic objects, and has also have uses in this fields as powder metallurgy. It is a process in which the particles of a powder are welded together by pressure and heating to a temperature below its melting point. The advantages of sintering are very high levels of purity with uniformity in starting materials, Capability to produce materials with controlled, uniform porosity, and preservation, due to the simpler subsequent fabrication process.

3.4 CHARACTERIZATION TECHNIQUE:

The different Characterization techniques that have been done in experiment are:

- X-ray diffraction(XRD)
- Scanning Electron Microscopy(SEM)
- UV-Visible spectroscopy
- Dielectric study

3.5 EXPLANATION OF DIFFERENT CHARACTERIZATION TECHNIQUE:

1. X-RAY DIFFRACTION (XRD):

X-rays are a form of electromagnetic radiation which have wavelength is in a range of 0.01 to 10 nms. The wavelengths are shorter than that of UV rays and longer than of gamma rays. X-ray diffraction is a common technique for the study of crystal structures and atomic spacing. XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. When x-rays are scattered from a crystal lattice, peaks of scattered radiation are observed which correspond to the following conditions: (i) the angle of incidence = angle of scattering. (ii) The path length difference is equal to an integer number of wavelengths. The condition of maximum intensity contained in Bragg's law above allows us to calculate details about the crystal structure.

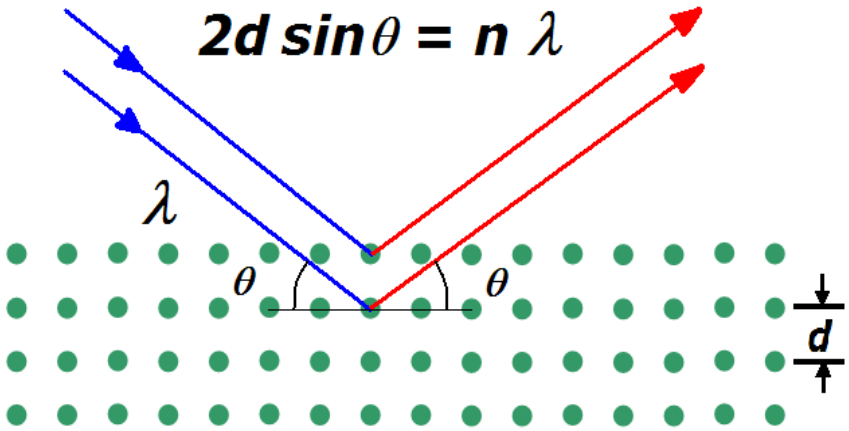


Figure 2: The Diffraction of X-rays by a family of lattice planes.

Bragg expressed this condition in an equation which is known as Bragg's Law with the equation

$$2d\sin\theta = n\lambda$$

λ = X-ray wavelength,

d = distance between lattice planes,

θ=angle of incidence with lattice plane

n = integer. XRD is done for to determine the crystallite size, crystal structure and to determine the phase composition of a material.

2. SCANNING ELECTRON MICROSCOPY (SEM):

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a different variety of signals at the surface of solid specimens. Accelerated electrons in an SEM carry significant amounts of kinetic energy and this energy are dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. The scattering of secondary electrons, backscattered electrons (BSE), and diffracted backscattered electrons are used to determine crystal structures and orientation of minerals and photons. Generally the Secondary electrons are commonly used for the determination of samples structures. Secondary electrons are important for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples. The signals that derive from electron-sample interactions give information about the sample including external morphology study and chemical composition.

3. UV-VISIBLE SPECTROSCOPY:

UV Visible spectroscopy measures the response of a sample with ultraviolet and visible range of electromagnetic radiations .A UV-visible spectrometer measures absorbance or transmittance from the UV range to which the human eye is not so sensitive to the visible wavelength range to which the human eye is sensitive. When radiation interacts with the matter, a number of processes can occur, including absorbance, transmittance, fluorescence, and photochemical reaction. Here, when measuring UV-visible the absorbance must to occur because light is a form of energy, and when it absorbs light by matter the energy content of the molecules increases. UV-visible spectra generally show only a few amounts of broad absorbance bands. UV-visible spectroscopy can also be used to determine many physicochemical characteristics of compounds and thus it can provide information about the identity of a particular compound.

4. DIELECTRIC STUDY:

Dielectric Spectroscopy is a powerful tool for investigating the transient species that occurs as intermediates in chemical and physical Processes. In particular, vital information could be obtained from microwave dielectric studies. A dielectric is an electrical insulator that can be polarized by an applied electric field. With external field application electric charges get polarized which causes the electric polarization. Due to dielectric polarization, there is a shift in positive charges towards the field and negative charges in the opposite direction for which it developsan internal electric field which reduces the overall field within the dielectric itself. The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy in materials. This study is very beneficial to explain various phenomena in electronics, optics, and solid-state physics. The dielectric properties of a substance such as dielectric constant, dielectric loss, relaxation time have provided an insight into the structure of the molecules of the system. Dielectric or electrical insulating materials are understood as the materials in which electrostatic filled can persist for a long time. These materials offer a very high resistance to the passage of electric current under the action of the applied direct-current voltage and therefore sharply differ in their basic electrical properties from conductive materials.

CHAPTER-4

RESULT AND DISCUSSION

1. XRDAnalysis

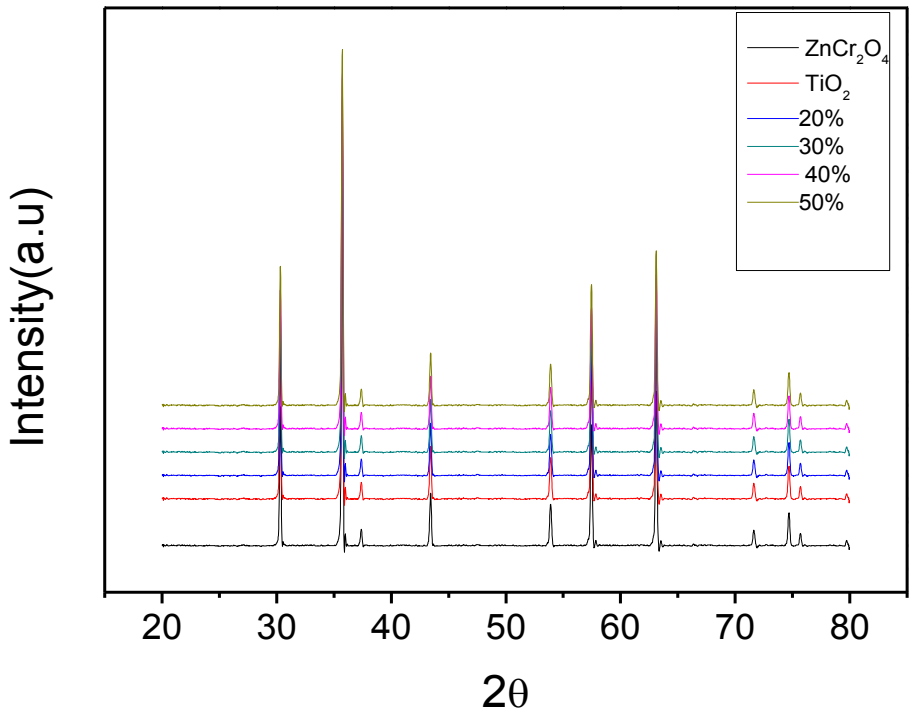


Figure 3: XRD pattern of (1-x) $ZnCr_2O_4$-xTiO_2 composite.

The XRD pattern of parent $ZnCr_2O_4$ confirmed the absolute single phase which was matched with JCPDS file no 22-1107. The XRD pattern of composite has found the presence of corresponding peaks of TiO_2 along with $ZnCr_2O_4$.This confirmed the perfect formation of composite of TiO_2 particle in matrix of $ZnCr_2O_4$.The major peaks of $ZnCr_2O_4$ has shifted towards higher diffraction angle. This indicates reduction in lattice parameter which implies the unit cell volume has been squeezed. As radius of Ti^{4+} ions is 60.5 and radius of Cr^{3+} ions is 61.5

and Zn^{2+} ion is 74 pm , so there is a possibility of Ti^{4+} ion substituting Cr^{3+} ion in octahedral sites.

2. SEM Analysis:

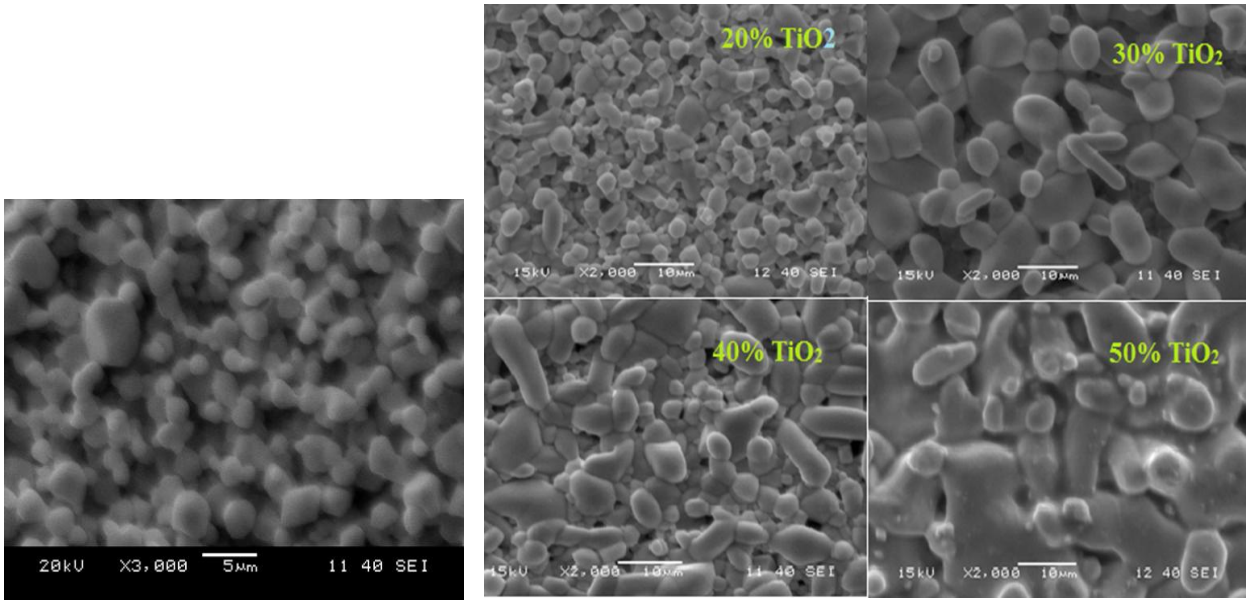


Figure 4: SEM image of (1-x) $ZnCr_2O_4$-xTiO_2 composite with different concentration i.e. x=0.2, 0.3, 0.4, 0.5.

The parent $ZnCr_2O_4$ sample contains identical grains size distributed uniformly throughout the sample. The presence of multipores indicates the sintering is not completed. With the weight percentage addition of TiO_2 to $ZnCr_2O_4$, the grain size increases in irregular manner and not uniformly. In 50 % TiO_2 addition the grain growth is not complete and seems to be in melted form. This grain growth has an impact on the electrical properties of the sample which we are going to discuss.

3. DIELECTRIC Analysis:

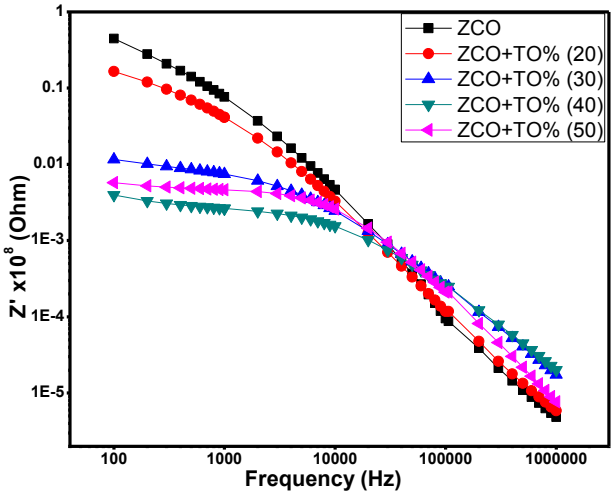


Figure-6

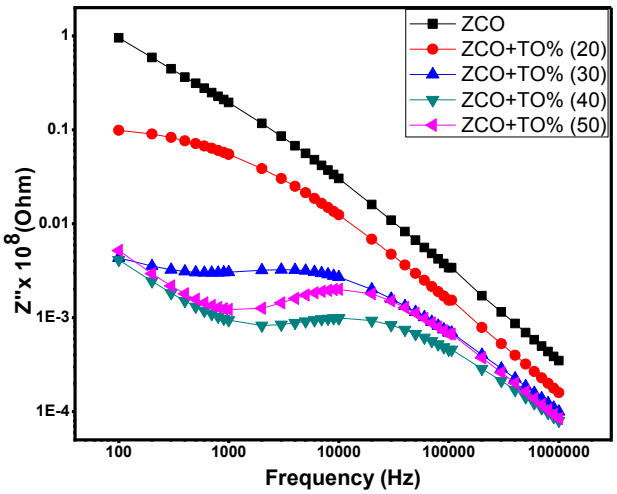
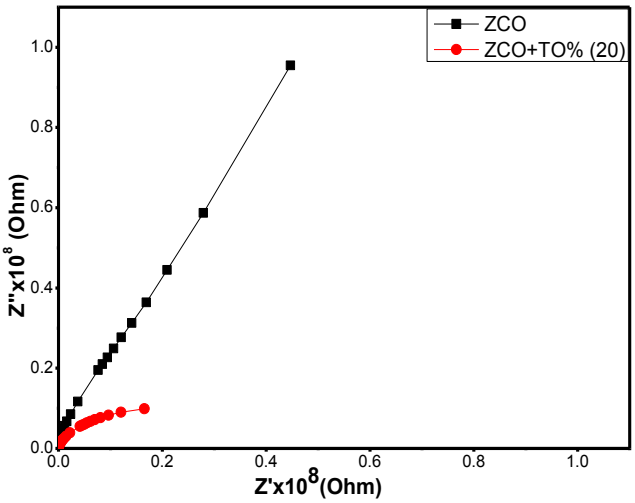


Figure-7

Figure no-6 and 7: Impedance of Composite (1-x) $ZnCr_2O_4$-xTiO_2composite with different concentration i.e. x=0.2, 0.3, 0.4, 0.5.

A polycrystalline sample contains many grains. Intra grain region is quite regular and order has no strong scattering centres (trapped charges or vacancies etc). That's why charge carriers can easily move which makes it a comparatively conducting region where as inter grain regions are irregular and disruptive in nature to charge carriers due to large presence of scattering canters. The grain boundary behaves as a resistive barrier. The matrix ZCO is characterised by small size of grains which results large grain boundaries. This contributes large impedance value of ZCO as we see in the plot. TiO_2 addition increases grain size which reduces grain boundary contributions as well as impedance. Conduction and polarisation mechanism are inter related as one promotes another. Hopping of free electrons at interstitial positions, hopping of ions through oxygen vacancies, exchange interaction between Cr^{3+} - Cr^{2+} is the major charge carriers which are responsible for conduction and polarisation mechanism. Various interfaces such as electrode – grain, grain- grain (grain boundary) are the dominating regions where these space charges accumulate which promotes polarisation.



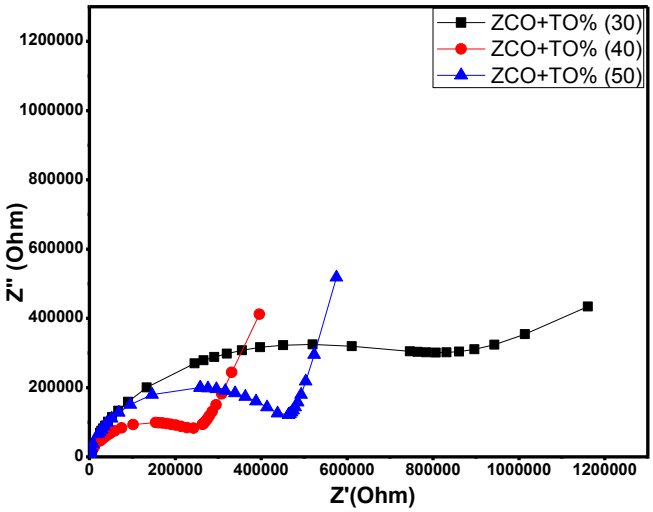


Figure-8 **Figure-9**

Figure 8, 9: Nyquist Semicircles of Composite (1-x) $ZnCr_2O_4$-xTiO_2 composite with different concentration i.e. x=0.2, 0.3, 0.4, 0.5.

Nyquist semicircles clarify idea about contributions of grains and interfaces. Each semicircle corresponds to one effect. The semicircles at higher frequency belongs to the grain effect, then to grain boundary and lastly to the electrode effect. The last two appears at comparatively lower frequencies. The radius of the semicircles proportional to the resistance of the region. The small one at high frequency side indicates the less resistive i.e. conducting nature belongs to grain effect. The spike may be the part of a large semicircle gives high resistive nature of grain boundary and electrode interface. The strong spike appears for ZCO indicates a large contribution from GB. The electrode effect cannot be avoided. For 20% TO, the arc seems to contain two overlapping semicircles a clear indication of both grain and grain boundary contribution. For next concentration of TO, contribution from three effects is cleared. The depressed semicircle represents the co-contribution of grain and GB effect where as the spike shows electrode polarisation as a role.

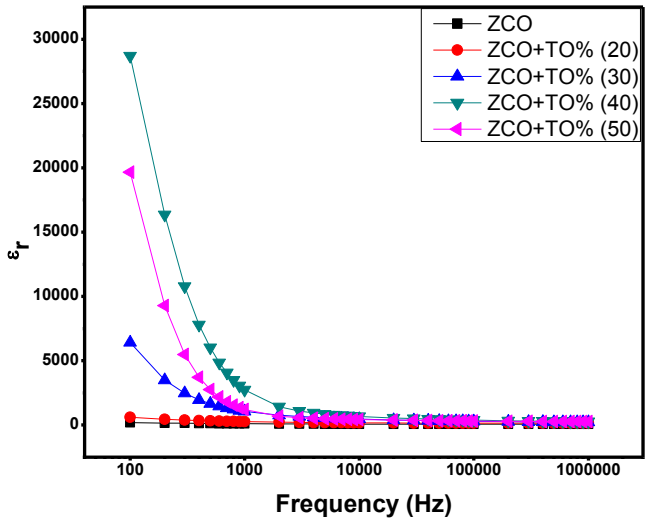


Figure-10

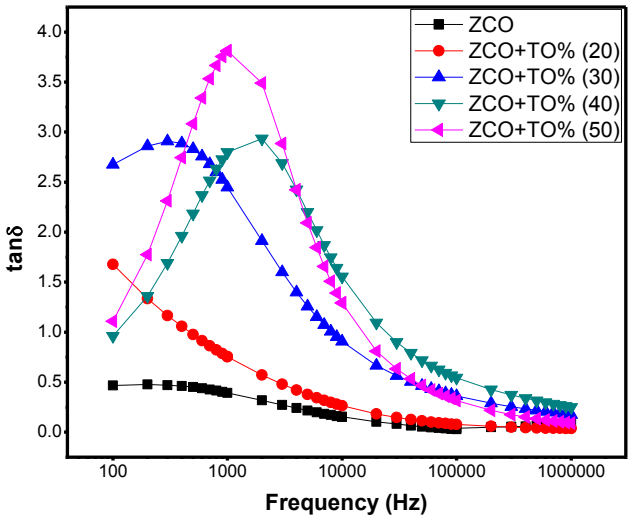


Figure-11

Figure 10 and 11: Dielectric constant and loss of Composite (1-x) $ZnCr_2O_4$-xTiO_2 composite with different concentration i.e. x=0.2, 0.3, 0.4, 0.5.

From the impedance study it is cleared that, conductivity with percentage addition of TO. This also reflects in the dielectric plot against frequency with drastic rise in value at 40% TO + ZCO at low frequencies. This indicates the contribution towards polarizability has been increased. Space charge polarisation is playing the key role in enhancing the relative permittivity of the material. Charge carriers through successful hopping reach towards different interfaces and pile up there as unable to cross the high resistive potential.

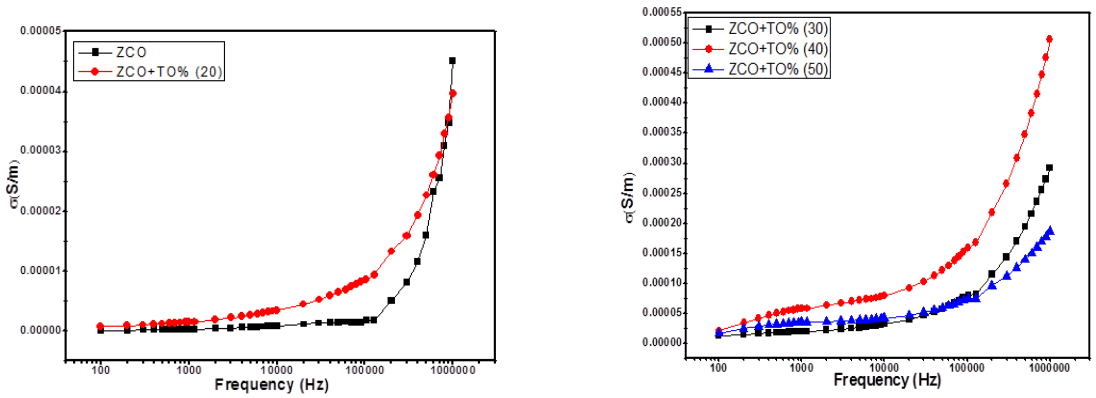


Figure 12: AC conductivity study of a plateau followed by a frequency dependent tail is observed in the Parent ZCO.

For 20% TO composite, same features observed except gradual variation of dc plateau to dispersive region. For next concentration of TO composite, a slow frequency variation part followed by a plateau and then a strong dispersive part is observed in the plots. The plateau portion means frequency independent gives the dc conductivity which arises due to the successful hopping mechanism of ions, electrons resulting a long range movement of charge carriers. The frequency dependent part of the curves represents the ac conductivity. This arises due to the unsuccessful hopping mechanism of ions, electrons resulting short range movement of charge carriers. Relaxation frequency is the inflection point of long rang to short range movement of charge carriers. Below relaxation frequency, successful hopping of charge carriers occurs which cause long range movement and beyond which unsuccessful hopping mechanism dominates. The gradual variation from dc plateau to ac dispersive region indicates the distribution of relaxation times. The non-uniformity of the grains is the reason behind this distribution times.

4. UV-Analysis:

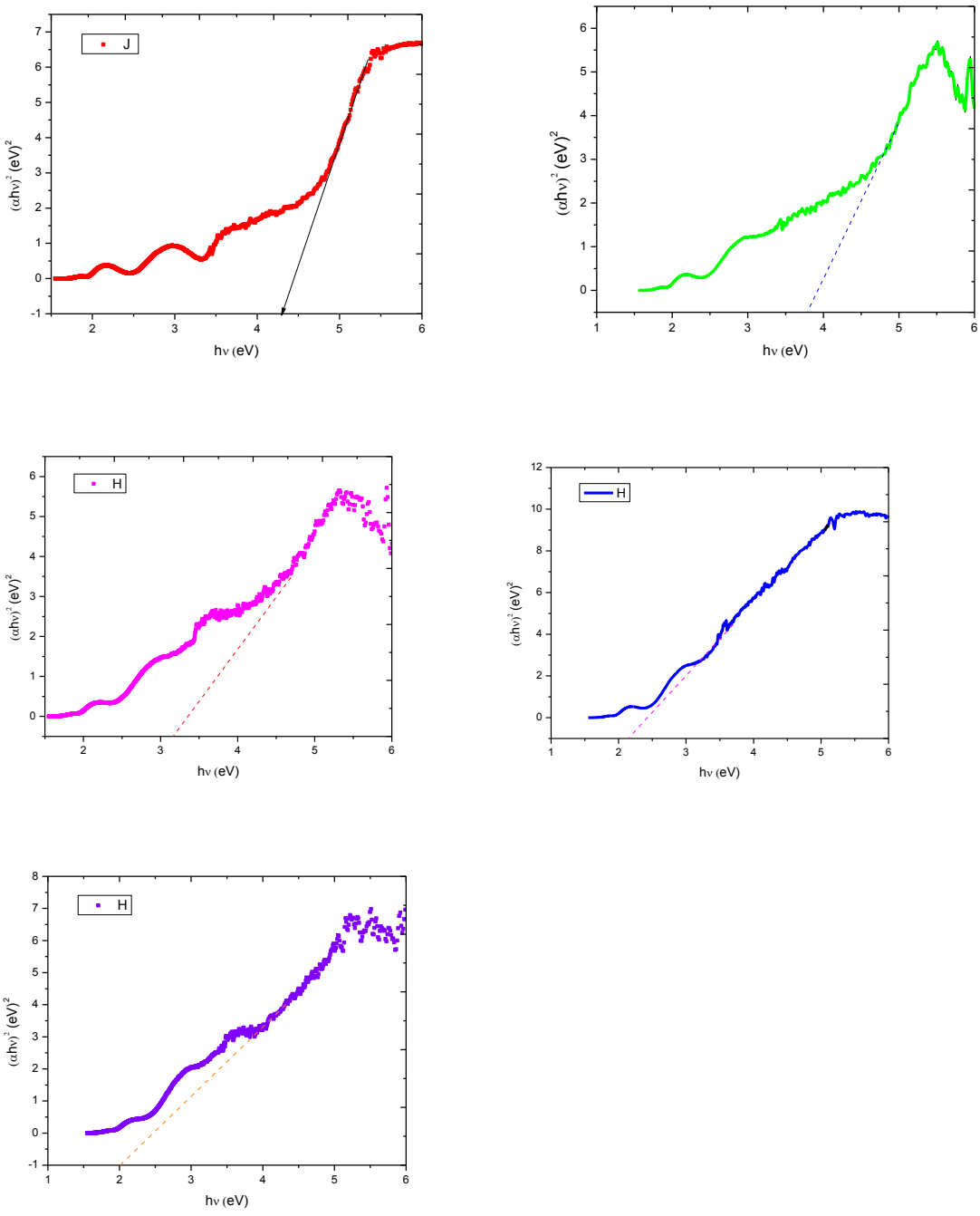


Figure 5: Band gap of (1-x) $ZnCr_2O_4$-xTiO_2 composite with different concentration i.e. x =0.2, 0.3, 0.4, 0.5.

The UV visible spectroscopy of the composite has been carried out to find out the band gap for ZCO-TO and various composite.

CHAPTER-5

CONCLUSION

- The electrical properties of ZCO-TO composite are studied properly by analysing the impedance data taken at RT within frequency windows of 100 Hz to 1 MHz.
- The presence of TO particles in the matrix of ZCO is confirmed from XRD study as it contains the peaks of both compounds. This indicates the formation of desired composite.
- SEM image shows the grain growth with percentage addition of TO. The size of the grain has put impact on the electric properties of the composite observed from impedance study.
- The impedance value decreases up to 40% addition of TO and then it increases again. Nyquist plots show the co contribution of grain and grain boundary with the electrode effect contributes towards conduction and polarisation mechanism.
- Space charge polarisation is responsible for rise in relative permittivity value.

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